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|--------------------------|------------------------|---------------------|--|
| Interview Summary | Application No. | Applicant(s) | |
| | 10/002,979 | MARUYAMA ET AL. | |
| | Examiner | Art Unit | |
| | Gregg Cantelmo | 1745 | |

All participants (applicant, applicant's representative, PTO personnel):

- (1) Gregg Cantelmo. (3) ____.
- (2) Mr. Harris A. Pitlick. (4) ____.

Date of Interview: 04 June 2007.

Type: a) ☐ Telephonic b) ☐ Video Conference
c) ☒ Personal [copy given to: 1) ☐ applicant 2) ☐ applicant's representative]

Exhibit shown or demonstration conducted: d) ☐ Yes e) ☐ No.
If Yes, brief description: ____.

Claim(s) discussed: All.

Identification of prior art discussed: All applied.

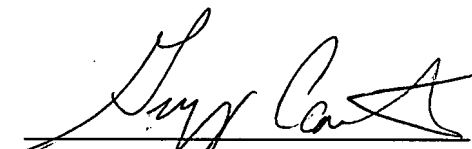
Agreement with respect to the claims f) ☐ was reached. g) ☒ was not reached. h) ☐ N/A.

Substance of Interview including description of the general nature of what was agreed to if an agreement was reached, or any other comments: See Continuation Sheet.

(A fuller description, if necessary, and a copy of the amendments which the examiner agreed would render the claims allowable, if available, must be attached. Also, where no copy of the amendments that would render the claims allowable is available, a summary thereof must be attached.)

THE FORMAL WRITTEN REPLY TO THE LAST OFFICE ACTION MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW. (See MPEP Section 713.04). If a reply to the last Office action has already been filed, APPLICANT IS GIVEN A NON-EXTENDABLE PERIOD OF THE LONGER OF ONE MONTH OR THIRTY DAYS FROM THIS INTERVIEW DATE, OR THE MAILING DATE OF THIS INTERVIEW SUMMARY FORM, WHICHEVER IS LATER, TO FILE A STATEMENT OF THE SUBSTANCE OF THE INTERVIEW. See Summary of Record of Interview requirements on reverse side or on attached sheet.

GREGG CANTELMO
PRIMARY EXAMINER


Examiner's signature, if required

Examiner Note: You must sign this form unless it is an Attachment to a signed Office action.

Continuation of Substance of Interview including description of the general nature of what was agreed to if an agreement was reached, or any other comments: Discussion was held with respect to a proposed amendment which further defines the anode material being a carbonaceous material. The Examiner indicated that the proposed claimed invention would be rendered obvious over the prior art of record without further evidence of patentability for the particular proposed claimed combination. Applicant's representative further provided an English translation of JP 04-190560 A which the examiner will make of record along with the interview summary.

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Request for examination: Not requested

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(Total 4 pages)

(54) Title of the invention:

Positive electrode active material for lithium secondary battery

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Specification

1. Title of the invention

Positive electrode active material for lithium secondary battery

2. Claim

5 A positive electrode active material for lithium secondary battery, characterized by being a lithium cobalt oxide represented by formula (I):



(wherein, x is 0 to 2, y is 0.001 to 0.4, and M represents an element or group of elements including at least Nb or Ta).

10 3. Detailed description of the invention

<Field of industrial application>

The present invention relates to a positive electrode active material for lithium secondary batteries, and more particularly, to a positive electrode active material for secondary batteries that dramatically improves the high-temperature storability of a secondary battery.

<Background art>

20 Sulfides such as titanium disulfide, molybdenum disulfide and the like have been conventionally proposed, among others, as positive electrode active materials for lithium secondary batteries, and some of [these sulfides] have been realized in practice.

In terms of obtaining batteries having a high energy density, however, such sulfide-based positive electrode active materials are problematic in that they afford low battery voltages, of 3 V or less. In order to obtain lithium secondary batteries having a higher energy density, thus, research has been carried out on using LiCoO_2 as a

positive electrode active material.

<Problem(s) to be solved by the invention>

When LiCoO_2 is used as the above positive electrode active material, battery voltages of about 3.9 to 4.5 V, higher than those of sulfide-based active materials, can be achieved, and a higher energy density is afforded. When Li is released from LiCoO_2 during battery charging, however, a problem arises in that part of the Co becomes CoO_2 , so that the instability of the tetravalent Co causes dramatic capacity deterioration after high-temperature storage.

For this reason, it has been proposed to use $\text{Li}_x(\text{CoFe})\text{O}_2$, in which Fe is present as a solid solution, in order to prevent capacity deterioration after high-temperature storage (Japanese Unexamined Patent Application Laid-open No. S63-211564).

However, using the above $\text{Li}_x(\text{CoFe})\text{O}_2$ still results in low capacity after high-temperature discharge, and hence there is scope for further enhancement of the high-temperature storage characteristic of the lithium secondary battery.

In light of the above problems, it is an object of the present invention to provide a positive electrode active material for lithium secondary batteries that dramatically improves high-temperature storability.

<Means for solving the problems>

The positive electrode active material for lithium secondary batteries of the present invention, which achieves the above goal, is characterized by comprising a lithium cobalt oxide represented by formula (I) below:



(wherein, x is 0 to 2, y is 0.001 to 0.4, and M represents an element or group of elements including at least Nb or Ta).

The present invention is explained in detail below.

5 The lithium cobalt oxide of the present invention represented by formula (I) can be easily synthesized by mixing and thermally treating lithium carbonate, a cobalt carbonate and an additive M (Nb or Ta), or through wet manufacturing, in which the additive M (Nb or Ta) and cobalt are mixed beforehand as a mixed carbonate, and
10 are then added to lithium carbonate, to be mixed therewith, followed by thermal treatment.

The additive M may be Nb or Ta, and may be used in the form of a metal powder, an oxide or a carbonate.

In the present invention, the value of the addition amount y of the
15 additive M in formula (I) above ranges preferably from 0.001 to 0.4. If the value of y is below 0.001, adding the additive affords no appreciable effect, which is undesirable in that sufficient prevention of capacity deterioration during high-temperature storage cannot be achieved; on the other hand, a value of y exceeding 0.4 results in a
20 smaller electric capacity caused by the addition of the additive M, which is undesirable.

Within the above-described range, the above additive M (Nb or Ta) is believed to stabilize the unstable CoO_2 after withdrawal of Li from the layer structure, while reducing simultaneously the
25 electrostatic repulsion among O^{2-} , during [battery] charging, thereby inhibiting crystal structure changes upon high-temperature storage.

The value of x in formula (I) is set to range from 0 to 2 since Li can vary freely within this range during charge and discharge, and hence any of the [range] values can be used herein.

5 Adding concomitantly Y, Ce or the like to Nb and Ta as the additive M, to yield for instance $\text{Li}_x(\text{CoNbY})\text{O}_2$, allows also providing a high-performance lithium secondary battery having the same effect as above.

10 As described above, using as the positive electrode active material of a lithium secondary battery the lithium cobalt oxide ($\text{Li}_x(\text{Co}_{1-y}\text{M}_y)\text{O}_2$) to which Nb or Ta has been added allows curbing capacity deterioration during high-temperature storage, which is highly valuable in industrial terms.

<Examples>

15 The present invention is explained in detail next by way of examples and comparative examples.

(Examples 1 to 3)

Various $\text{Li}_x(\text{Co}_{1-y}\text{Nb}_y)\text{O}_2$ [oxides] were synthesized in accordance with the formulations given in Table 1.

20 Firstly, predetermined amounts of Li_2CO_3 and $2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and Nb_2O_5 were added and were thoroughly mixed, after which the mixture was pressure-molded and was made to react through heating at 900°C for 12 hours in air ($\text{N}_2/\text{O}_2 = 80/20$), to yield a lithium cobalt oxide.

25 Using the obtained lithium cobalt oxide as a positive electrode active material, thereto were added graphite, as an electroconductive auxiliary agent, in a proportion of 6wt%, and polytetrafluoroethylene,

as bonding agent, in a proportion of 4wt%; after mixing of the whole, [the resulting mixture] was pressure-molded under 4 t/cm², to manufacture a round-plate molded body having a diameter of 15 mm and a thickness of about 0.7 mm.

5 Fig. 1 illustrates the battery (test cell) manufactured using this positive electrode. In the figure, the reference numeral 1 denotes a negative electrode, 2 denotes a positive electrode, 3 denotes a separator (electrolyte), 4 denotes a seal material, 5 denotes a terminal, 6 denotes a positive electrode-side case, and 7 denotes a negative electrode-side case. As the negative electrode 1 was used a negative electrode having a diameter of 15 mm, punched out of a Li-Al alloy tape (Al: 15wt%). As the separator 3 was used a separator comprising a polypropylene nonwoven fabric and, as the electrolyte (nonaqueous electrolyte), was used a 1 mol/l solution of LiBF₄ in a 10 1:1 volume ratio mixed solvent of propylene carbonate and 1,2-dimethoxyethane.

15 (Examples 4 to 6)

 Various $\text{Li}_x(\text{Co}_{1-y}\text{Ta}_y)\text{O}_2$ [oxides] were synthesized in accordance with the formulations given in Table 1, and then lithium secondary batteries were manufactured as described above.

20 (Examples 7 and 8)

 Lithium cobalt oxides were prepared by adding Y and Ce to $\text{Li}_x(\text{Co}_{1-y}\text{M}_y)\text{O}_2$ to yield $\text{Li}(\text{Co}_{0.9}\text{Nb}_{0.05}\text{Y}_{0.05})\text{O}_2$ and $\text{Li}(\text{Co}_{0.9}\text{Ta}_{0.05}\text{Ce}_{0.05})\text{O}_2$ after which lithium secondary batteries were manufactured as described above.

25 (Comparative examples 1 and 2)

Lithium secondary batteries were manufactured as in the examples but using herein as the positive electrode active materials LiCoO_2 and $\text{Li}(\text{Co}_{0.9}\text{Fe}_{0.2})\text{O}_2$ according to a conventional technology.

5 The charge-discharge capacity values of the various batteries before and after storage are given in Table 1.

Battery charge and discharge was carried out within a voltage range of +3.0 to +4.3V and a charge current and discharge current per unit cross section area of the positive electrode of 1.0 mA/cm^2 .

10 Charge-discharge cycles were carried out first, whereupon the charge capacity value after 5 cycles was recorded in Table 1 as the charge-discharge capacity before storage; next, the batteries were stored at 60°C for 7 days, after which charge-discharge cycles were carried out, whereupon the charge capacity value after 3 cycles was recorded in Table 1 as the charge-discharge capacity after storage.

15 Table 1

| Battery | Positive electrode material form | Charge-discharge capacity before storage (Wh/kg) | Charge-discharge capacity after storage at 60°C for 7 days (Wh/kg) |
|-------------|--|--|--|
| Example 1 | $\text{Li}(\text{Co}_{0.95}\text{Nb}_{0.05})\text{O}_2$ | 460 | 295 |
| Example 2 | $\text{Li}(\text{Co}_{0.9}\text{Nb}_{0.1})\text{O}_2$ | 457 | 294 |
| Example 3 | $\text{Li}(\text{Co}_{0.7}\text{Nb}_{0.3})\text{O}_2$ | 452 | 281 |
| Example 4 | $\text{Li}(\text{Co}_{0.95}\text{Ta}_{0.05})\text{O}_2$ | 461 | 264 |
| Example 5 | $\text{Li}(\text{Co}_{0.9}\text{Ta}_{0.1})\text{O}_2$ | 455 | 263 |
| Example 6 | $\text{Li}(\text{Co}_{0.7}\text{Ta}_{0.3})\text{O}_2$ | 446 | 246 |
| Example 7 | $\text{Li}(\text{Co}_{0.9}\text{Nb}_{0.05}\text{Y}_{0.05})\text{O}_2$ | 455 | 295 |
| Example 8 | $\text{Li}(\text{Co}_{0.9}\text{Ta}_{0.05}\text{Ce}_{0.05})\text{O}_2$ | 460 | 265 |
| Comparative | LiCoO_2 | 461 | 0 |

| | | | |
|-----------------------|---|-----|----|
| example 1 | | | |
| Comparative example 2 | $\text{Li}(\text{Co}_{0.9}\text{Fe}_{0.2})\text{O}_2$ | 458 | 80 |

The above results show that adding Nb and Ta enhances substantially the high-temperature storage characteristic. The same effects are achieved even when impurities such as Y, Ce or the like are added.

<Effect of the invention>

As explained above, the present invention uses lithium cobalt oxides to which Nb or Ta are added, and hence the invention allows dramatically improving the high-temperature storage characteristic of lithium secondary batteries, thereby expanding the range of application of secondary batteries.

4. Brief description of the drawings

Fig. 1 is a schematic diagram of a lithium secondary battery according to the present example. In the figure, 1 is a negative electrode, 2 is a positive electrode, 3 is a separator (electrolyte), 4 is a seal material, 5 is a terminal, 6 is a positive electrode side case and 7 is a negative electrode side case.

Figure 1

- 1 negative electrode
- 2 positive electrode
- 3 separator, electrolyte
- 4 seal material
- 5 terminal

6 positive electrode side case

7 negative electrode side case